**C - 8**

# THE AGING TIME EFFECT ON THE N-DOPED $TiO_2$ CRYSTAL STRUCTURE FOR DYE-SENSITIZED SOLAR CELLS

**Kusumawardani C[1*], Sugiyarto KH[1], Prodjosantoso AK[1] and Mingmei**

[1] *Department of Chemistry, Yogyakarta State University, Yogyakarta, Indonesia, 55281*
[2] *School of Chemistry & Chemical Engineering, Sun Yat-sen University, Guangzhou, China, 510275*
[*] *Corresponding author: cahyorini.k@uny.ac.id, irienuny@yahoo.com*

**Abstract**

The synthesis of N-doped titanium oxide (N-doped $TiO_2$) have been undertaken through the hydrolysis of titanium isopropoxide with the existence of dodecylamine as nitrogen source. Aging time was applied as post synthesis treatment to facilitate a better interaction between nitrogen and titanium to obtain high nitrogen content on the $TiO_2$ framework. The mesoporous formation might also take place during the aging time treatment, which were done for 1 – 6 days after the hydrolysis process finished, and continued by filtering process to produce the N-doped $TiO_2$. The resulted materials were then calcined at the temperature of 450 $^oC$ for 4 hours. X-ray diffraction (XRD) analysis of calcined N-doped $TiO_2$ revealed that the aging time treatment affects the crystallization of the N-doped $TiO_2$. Porosity analysis results also indicates that the mesopore formation has a highly dependent on the aging time treatment with the highest surface area are given by aging time of 5 days. The aging time variation also influence the visible-light absorption leaded to the different band gap energy values. The N-doped $TiO_2$ aged for 3 days provided the best photoactivity on the dye-sensitized solar cells (DSSCs) system with the overall efficiency of 3.1%.

**Key words**: Aging time, N-doped $TiO_2$, DSSC, photoactivity key, words

## INTRODUCTION

The development of alternative renewable energy technologies is one of crucial importance for the world sustenance since the highly demand onto fossil energy lead to many environmental problems. Fossil fuels are nonrenewable and likely not continue to remain abundant for future generations (Argazzi *et al.*, 2004). Photovoltaic technology is one of potential solutions to the energy challenge by directly convert the solar energy to electricity. Dye-sensitized solar cells (DSSCs) based on Titanium Oxide semiconductor have been widely investigated as a promising photovoltaic technology because of its low production cost and simple structure (O'regan and Gratzel, 1991). Despite low cost DSSCs had achieved an overall efficiency of around 12%, a level that is not easily obtained since the first concept noticed in early 1970. In order to commercialize DSSC, it is necessary to improve the light-to-electricity conversion efficiency. Some efforts have been devoted to develop the more efficient dyes but the $TiO_2$ semiconductor modification to obtain the most efficient for dye support have been overlooked.

Titanium oxide is one of powerful semiconductors that easily to produce, inexpensive and shown good stability under illumination in most environments (Mills and Hunte, 1997; Linsebliger *et al.*, 1995). However, the wide band-gap nature of $TiO_2$ which is around 3 – 3.4 eV

only allows $TiO_2$ to adsorb UV light –merely 5% of the incoming solar energy on the earth's surface– impairs $TiO_2$ from playing such an important role (Qiu and Burda, 2004). To improve the $TiO_2$ response towards light, it is desirable to red-shift the absorption onset to also include the less energetic but more intense visible part of the solar spectrum (Horikawa *et al*., 2008). In DSSC system, this has been achieved by using dye sensitizers for harvesting the visible light but the problems come from the long term stability of the dyes (Gratzel, 2000; Nazeeruddin *et* al., 1993). The use of pure $TiO_2$ semiconductors, which there is some oxygen deficiency in the crystal structure can create electron-hole pairs (Ihara *et al*., 2003; Sathish *et al*., 2005; Chen *et al.*, 2005; Burda *et al.*, 2003) and that the oxidizing holes can either react with the dye and destroy it and/or is scavenged by iodide ions (Chen *et al*., 2007), may lead to shorten the lifetime of the dye-sensitized solar cells. To solve these problems, we introduce nitrogen-doped $TiO_2$ due to the replacement of pure $TiO_2$ into the DSSC system to enhance the energy conversion efficiency.

Nitrogen-doped $TiO_2$ have been prepared through several ways, but mainly it obtained using high temperature treatment of $TiO_2$ under N atmosphere (Asahi *et al*., 2001; Irien *et al*., 2003) and sol gel method (Qiu and Burda, 2007; Linsebliger *et al.,* 1995) because it affords simplicity in controlling the nitrogen doping level and particle size by simple variations in experimental condition, such as hydrolysis method, solution pH and solvent systems (Burda *et al*., 2003). In sol gel process, it is easily to control the pore and crystal formations by applying aging time and calcination treatments. Those process may occur separately or simultaneously depend on the applied treatment (Zhao *et al*., 2008). In this article, we report the influence of aging time that applied during sol gel synthesis process on the crystal structure of nitrogen-doped $TiO_2$ and also the study of its application in DSSCs system.

## RESEARCH METHOD

### Materials and Methods

***Materials***. Titanium Tetra Isopropoxide, $Ti(OPr)_4$ 97%, dodecylamine, $Cd(NO_3)_2$ 9 $H_2O$ and $(NH_4)_2S$ were purchased from Aldrich. Acetylacetone, and TritonX-100 were purchased from Fluka. Ethanol absolute and $CH_3COOH$ were obtained from Merck. N719, electrolyte EL-HSE, TEC 15 electrode glass plate and Pt-coated counter electrode are commercial products of Dyesol (Australia). All materials were used as received.

***Synthesis of N-doped $TiO_2$.*** The N-doped $TiO_2$ was synthesized following previous procedure (Kusumawardani *et al.*, 2010) as follow: a mixture of 3 mL of $Ti(OPr)_4$, 10 mL dodecylamine, and 80 mL of ethanol absolute solution were refluxed for 4 hours at 70 $^oC$ until getting a clear solution. This solution was cooled to room temperature and added by $CH_3COOH$ to obtain the pH of 3.5. Hydrolysis process was then achieved by adding 20 mL of deionized water dropwise into the solution under vigorous stirring, the solution continues stirred for 24 hours. The aging time was applied to the hydrolysis result and varied for 0, 1, 2, 3, 4, 5, and 6 days. The resulting yellowish precipitate were centrifuged and washed subsequently with distilled water and ethanol. Finally, the N-doped $TiO_2$ were vacuum-dried and calcined at a heating rate of 2 $^oC$/min in air atmosphere for 4 hours at 450 $^oC$.

***Characterization.*** The resulting N-doped $TiO_2$ powders were analyzed using X-Ray powder diffractometer (XRD, Rigaku), $N_2$ adsorption-desorption (NovaWin 2000, Quantachrome), UV-visible diffuse reflectance spectrophotometer (UV-2550, Shimadzu) and applied as fotoanode in DSSC system.

Crystallite size was calculated by applying Sherrer's equation:

$$d = \frac{0.9\,\lambda}{\beta cos\theta}$$

where, $d$ is the crystalline size, $\lambda$ is the wavelength of the CuK $\alpha$ (1.54 A$^o$), $\theta$ is the angle between

the incident beam and the reflecting lattice plane and $\beta$ is the full width at half maxima (FWHM) of the diffraction peak (in radian).
Lattice constant was calculated by applying the formula:

$$a = d(h^2 + k^2 + l^2)$$

where, $a$ is lattice constant, $d$ is interplanar spacing and $h$, $k$, $l$ are lattice planes. Interplanar spacing was calculated by applying the formula:

$$d = \lambda/2\, Sin\, \theta$$

where, $\theta$ is the angle between the incident beam and the reflection lattice planes.
The energy band gap was calculated by employing direct formula

$$E_g\ (eV) = 12397.8 / \lambda max\ (\text{Å})$$

where, $E_g$ 0 is an energy band gap and $\lambda_{max}$ is the wavelength at which maximum absorption was shown.

***Synthesis of N-doped $TiO_2$ thin film.*** The N-$TiO_2$ thin film is prepared on *Indium Tin Oxide* (ITO) using procedure: a reverse micellar solution of 0.2 M Triton X-100 and 0.4 M water was prepared in acetyl acetone. To this solution we added 1 gr N-$TiO_2$ powder under vigorous stirring and at ambient conditions resulted N-$TiO_2$ paste. The paste was then coated on 1 $cm^2$ ITO glass, the film was then slowly heated in air up to 450 °C for two hours.

***DSSC Fabrication and Characterization.*** To fabricate the DSSCs, the N-doped $TiO_2$ thin film were immersed in 0.3mM solution of N719 dye in acetoneitrile overnight. Cells were assembled by placing the Pt-counter electrode (CE) over the active area of N-doped $TiO_2$ working electrode. The electrolyte was introduced through drilled hole on CE by capillary action, the hole was then sealed. DSSC efficiency has been determined by current-voltage measurement that performed using computerized control of Keithley instrument with a 450 W Xenon lamp, which was focusing to provide 1000 W/$m^2$, equivalent to one sun at AM 1.5 at the surface of the cells. The instrument was calibrated using silicon diode. The spectral output of the lamp was matched in the region 350-800 nm with the aid of a Schott KG-5 sunlight filter so as to reduce the mismatch between the simulated and the true solar spectrum to less than 2%. The current-voltage characteristics of the cells were determined by biasing the cells externally and measuring the generated photocurrents. The overall photo-conversion efficiency, $\eta$ is calculated from the integral of photocurrent density ($I_{sc}$), the open circuit photocurrent ($V_{oc}$), the fill factor of the cell (*ff*), and the intensity of incident light ($I_s$) using the formula

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{inc}}.100\%$$

With $V_{pp}$= maximum voltase (V); $I_{pp}$= maximum current (mA/$cm^2$); $I_{sc}$ = short current (mA/$cm^2$); $V_{oc}$= *open circuit* and $P_{inc}$ = light intensity (W/$cm^2$). Fill factor (*ff*) is given by

$$FF = \frac{P_{\max}}{V_{oc} I_{sc}} = \frac{V_{PP} I_{PP}}{V_{oc} I_{sc}}$$

where $V_{pp}$ is a maximum voltage and $I_{pp}$ is a maximum current.

## RESULT AND DISCUSSION

N-doped $TiO_2$ have been prepared through sol gel method by hydrolysis of N-substituted titanium isopropoxide precursors in alcohol solution. The process was included reflux treatment to facilitate a better interaction between titanium and nitrogen atoms from amine group of dodecylamine. It found that complexation of organic amines on the Ti metal center creates highly

efficient precursors to result high doping level of N-doped $TiO_2$ nanoparticles (Kusumawardani, 2010). Beside high doping level, this method also easy to control the structure and high surface area by controlling the synthesis parameters. In sol gel method to synthesis nanoparticle mesopore material, the crystal growth and pore formation are two different processes that happen during the synthesis. These method are playing important role on structure properties of the resulting materials. As doping process also take a significant place in this synthesis method, beside reflux treatment aging time is another treatment to provide a higher doping level on the N-doped $TiO_2$ (Gole *et al.*, 2003). The aging time treatment also influence the structure and pore properties of N-doped $TiO_2$ nanoparticles.

The crystal structures of the synthesized N-doped $TiO_2$ were studied using X-ray powder diffraction (XRD) and the diffractograms were shown in Figure 1. The peaks in all difractograms indicated the existence of anatase and rutile phases except the synthesis without aging time treatment. It means that there was phase transition happened during the aging time since no rutile crystal phase on the N-doped $TiO_2$ synthesized without applying aging time treatment. The crystallite sizes of N-doped $TiO_2$ were determined from the half-width of the main peaks using the Scherrer formula (Chi *et al.*, 2007). The structure properties of N-doped $TiO_2$ that synthesized from aging time treatment variation are listed in Table 1. It can be seen that aging time treatment have influenced the crystal structure of N-doped $TiO_2$ even it didn't provided a specific trends into particle size and lattice parameter.

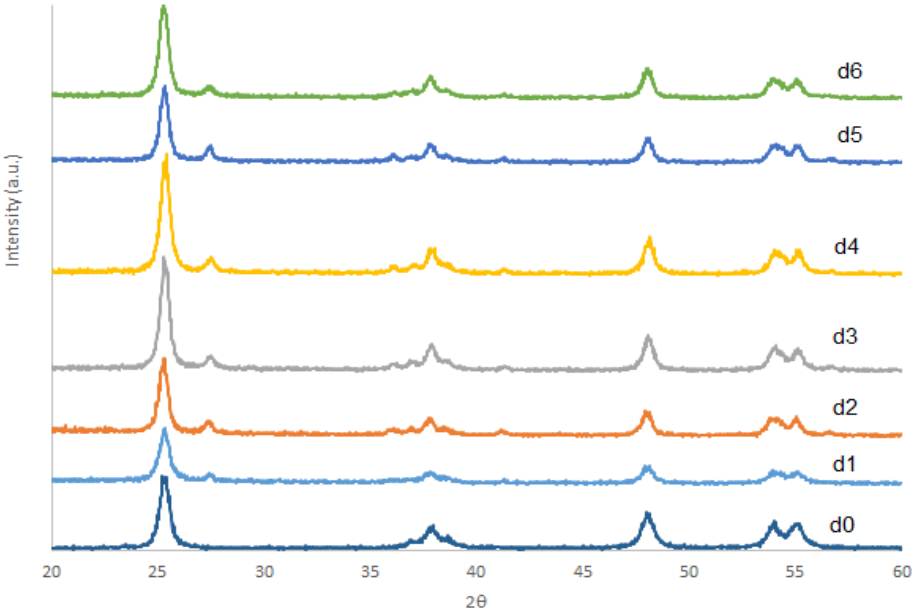


Figure 1 XRD diffractogram of N-doped $TiO_2$ synthesized on the variation of aging time (d = day)

Table 1 The effect of aging time on the N-doped $TiO_2$ structures

| Character | | Aging Time (days) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
| *a* | Å | 3.7832 | 3.7924 | 3.7933 | 3.8032 | 3.8112 | 3.8091 | 3.8153 |
| *c* | Å | 9.5121 | 9.5175 | 9.5223 | 9.5214 | 9.5232 | 9.5267 | 9.5344 |
| *L* | nm | A:10.6 | A:9.4 R:12.6 | A:12.1 R: 13.2 | A:12.9 R:14.4 | A:13.1 R:15.2 | A:10.6 R:11.7 | A:10.4 R:12.1 |
| $S_{BET}$ | $m^2g^{-1}$ | 88,3 | 101.2 | 119,5 | 122.4 | 167.3 | 177.2 | 112.7 |
| $D_{BJH}$ | Nm | 3.8 | 4.6 | 4.9 | 4.7 | 5.0 | 5.1 | 6.7 |
| $E_g$ | eV | 2.98 | 2.95 | 2.92 | 2.85 | 2.81 | 2.78 | 2.72 |

*a*, *c* : lattice parameter of anatase phase structure
*L* : crystal size, A: anatase, R: rutile
$S_{BET}$ : specific surface area
$D_{BJH}$ : average BJH pore diameter

The relation between aging time and crystal phase of N-doped $TiO_2$ (Figure 2) showed that the longer aging time provided the higher rutile crystal phase that might be caused by phase transition during the aging time. The transition phase are possibly happened since the particle and nucleation growths are happened simultaneously during the aging process as, also reported by Ito *et al.*, 2000 on synthesis of meso-macroporous anatase $TiO_2$. The use of dodecylamine in the synthesis, instead of being nitrogen source also played important role as stabilizing agent to avoid fast particle growth that leads to the formation of rutile crystal phase during the hydrolysis process. In the synthesis without aging time treatment, there was no rutile phase structure found in the resulting material. Dodecyalmine had effectively prevent the hydrolysis process to form the rutile structure, which is thermodynamically more stable than anatase. In the aging process, the dodecylamine didn't played the main role as stabilizing since it already dispersed in the N-doped $TiO_2$ framework, but played as templating agent for pore formation (Kusumawardani, 2012). It was difficult to prevent the phase transition of anatase crystal structure changed to rutile phase since there was no hindrance of fast particle and nucleation growths during the aging time treatment. So, the longer aging time leaded the more formation of rutile crystal phase of N-doped $TiO_2$, but the lower rutile crystal phase appeared on the N-doped $TiO_2$ with aging time of 6 days.

The calcination treatment also influenced the crystal phase transition since the crystal growth is having highly dependent on the sintering temperature. Rutile is easily formed by calcining the N-doped $TiO_2$ at temperature above 500 $^oC$, as also reported by Zhao *et al*., 2008. The crystallization process is faster when the calcination was done in air atmosphere because the existence oxygen affects the framework arrangement of $TiO_2$ crystal. The low rutile crystal phase from 6 days aging time may be caused by more stable anatase phase crystal formed from the aging treatment so lesser phase transition during calcination treatment. The more stable anatase that prevent the phase transition during calcination process was also reported by Yanagisawa and Ovenstone, 1999 that using hydrothermal technique to synthesize anatase crystal.

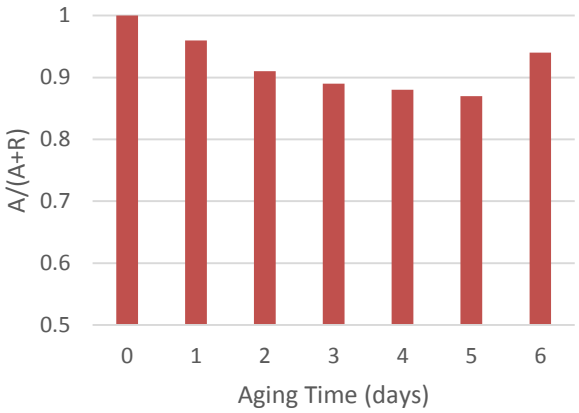


Figure 2 Anatase to Rutile Ratio of N-doped $TiO_2$

The influence of aging time treatment on the porosity of resulted N-doped $TiO_2$ have been studied using $N_2$ Gas Sorption Analysis. The nitrogen adsorption-desorption isotherm curves of N-doped $TiO_2$ and its corresponding pore radius distribution are shown in Figure 3 and 4. All adsorption desorption curves exhibited type-IV isotherm with an H2 hysteresis loop according to IUPAC classification (Rouquerol *et al*., 1999), which means that all prepared materials have mesoporous structure.

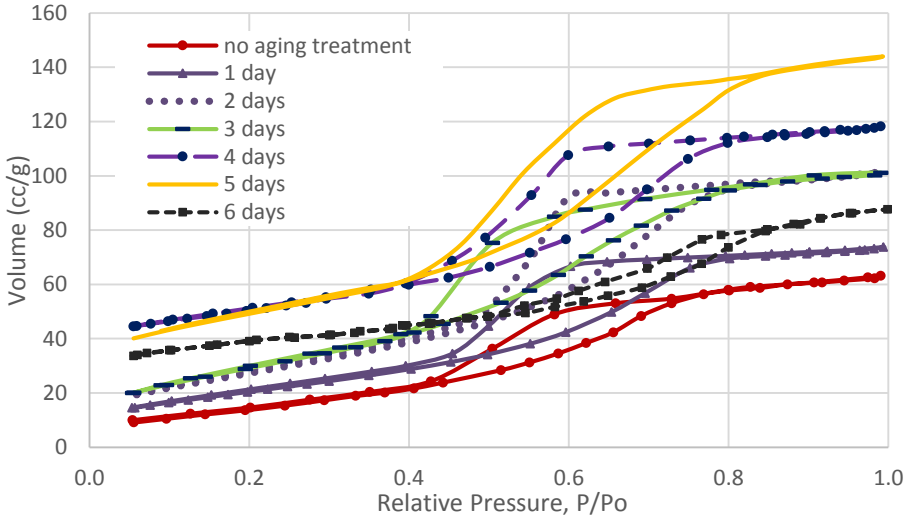


Figure 3. Isotherm curve of N-doped $TiO_2$

The porosity properties of N-doped $TiO_2$ are listed in Table 2. It showed that aging time treatment are giving significant influence on surface area and pore radius distribution of resulting materials. The effect of aging time treatment on the pore structure of N-doped $TiO_2$ indicated that the formation of pore structure and crystal structure are occurred simultaneously during the aging time. The N-doped $TiO_2$ without aging time treatment has a mesopore structure with two peaks pore size distribution, while the materials that synthesized with aging time treatment provided one sharp peak centered at 3 – 8 nm. That means that aging time leaded to the formation more homogenous mesopores and also tend to result higher surface area. The highest surface area are given by N-doped $TiO_2$ synthesized with aging time of 5 days, which is 177 $m^2/g$ and showed a sharp pore radius peak centered at 5.1 nm.

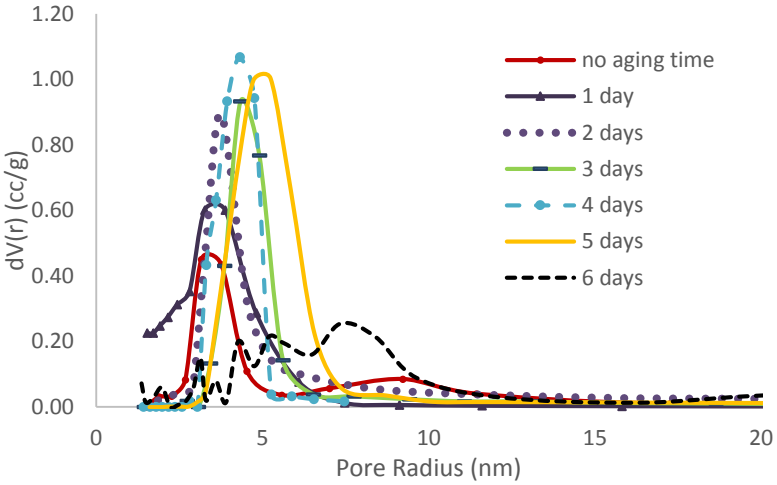


Figure 4. Pore size distribution of N-doped $TiO_2$

The optical absorbance and reflectance were used to study the electronic structure of the N-doped $TiO_2$ nanoparticles. The yellowish N-doped $TiO_2$ sphere powders show good absorbance of visible light. It can be seen from Figure 4 that the visible light absorption is high and extended up to 550 nm in the case of N-doped $TiO_2$ calcined at 450 $^oC$. The absorption shift may be due to the existence of nitrogen species occupy some of the oxygen positions in the lattice. This also rules out the occupancy of N in any other positions such as interstitial sites, which should give rise to a mid-gap band/level between valence and conduction bands. The band gap energy calculated by the equation above indicated that the aging time resulted the N-doped $TiO_2$ with lower band gap energy. It may be caused by the higher nitrogen doped on $TiO_2$ framework after the aging time. The higher nitrogen content on $TiO_2$ provided the more visible light active material. This means that the nitrogen doping process also occurred during the aging time treatment.

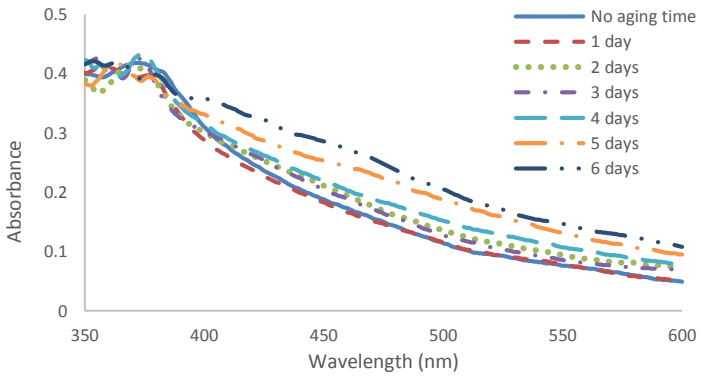


Figure 5. UV-Visible Spectra of N-doped $TiO_2$ synthesized with aging time variation

Figure 6 shows the current-voltage curves of the open cells based on the resulted N-doped $TiO_2$ photoelectrodes. A pronounced increase in the photocurrent for the DSSC based on the nitrogen-doped titania synthesized with aging time treatment was observed. The performance parameters of the DSSCs are summarized in Table 2. A high energy conversion efficiency were achieved from the DSSC based on N-doped $TiO_2$ with aging time treatment than the DSSC based on N-doped $TiO_2$ without aging time. It assumed that visible light absorption of nitrogen-doped

$TiO_2$ supports intrinsically increases the efficiency value due to the photoresponse of N-doped $TiO_2$ in the visible light region, which is also supported by the results reported by Kusumawardani *et al.*, 2010; Lindgren *et al.* and Ma *et al.*, 2005. They have demonstrated that the photoinduced current due to the visible light activity of the best N-doped $TiO_2$ electrode prepared by reactive DC magnetron sputtering can increase significantly by approximately 200 times over those of the undoped $TiO_2$ electrodes. On the basis of these results, it can be expected that the optimization the amount of nitrogen doping in titania nanoparticles and electrode can further improve the performance of the DSSCs.

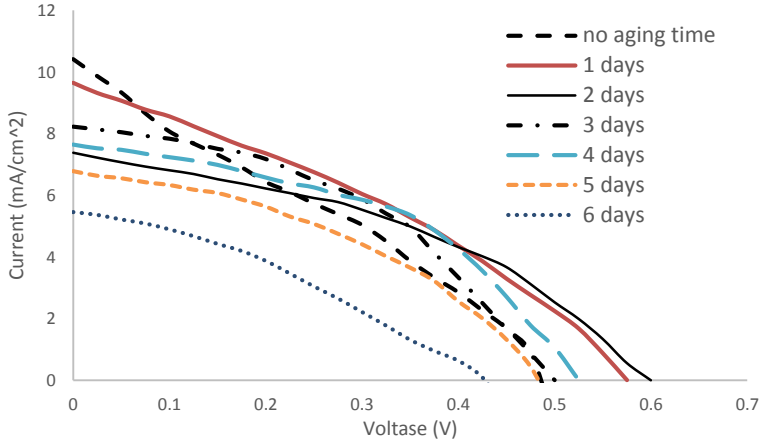


Figure 5. I-V characteristic of DSSCs based on N-$TiO_2$ synthesized with aging time variation

Table 2. I-V characteristic of DSSCs based on N-doped $TiO_2$

| | $I_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $I_{pp}$ (mA/cm$^2$) | $V_{pp}$ (V) | ff (%) | η (%) |
|---|---|---|---|---|---|---|
| No aging time | 10.42 | 0.50 | 6.94 | 0.425 | 0.57 | 2.8 |
| 1 day | 9.65 | 0.575 | 5.28 | 0.35 | 0.33 | 1.9 |
| 2 days | 7.38 | 0.60 | 4.99 | 0.45 | 0.51 | 2.3 |
| 3 days | 8.23 | 0.45 | 7.86 | 0.40 | 0.85 | 3.1 |
| 4 days | 7.65 | 0.525 | 4.87 | 0.375 | 0.46 | 1.8 |
| 5 days | 6.78 | 0.475 | 5.52 | 0.45 | 0.77 | 2.4 |
| 6 days | 5.45 | 0.425 | 3.87 | 0.35 | 0.59 | 1.4 |

## CONCLUSION AND SUGGESTION

The N-doped $TiO_2$ nanocrystalline materials were chemically synthesized by sol gel method by applying aging time treatment. It was observed that the aging time treatment has a highly significance effects on the crystal structure of the resulting N-doped $TiO_2$, i.e crystal phase, particle size, lattice parameter, porosity and the structure electronic. As the consequence, it also influences the photoactivity of the N-doped $TiO_2$ when they applied in the dye-sensitized solar cells. The photoactivity of the DSSC based on the N-doped $TiO_2$ was in agreement with the corresponding optical spectrum. The highest energy conversion efficiency was achieved successfully for the DSSC based on the nanocrystalline N-doped $TiO_2$ electrode aged for 3 days.

## REFERENCES

Asahi, R., Morikawa, T., Aoki, K., and Taga, Y. (2001). Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*. 293, 269-273

Argazzi, R.; Murakami, I.N.Y.; Zabri, H.; Odobel, F.; Bignozzi, C.A. (2004). Design of Molecular

Dyes for Apllication in Photoelectrochemical and electrochromic devices based on nanocrystalline metal oxide semoconductors. *Coord. Chem. Rev.* 248, 1299-1316

Burda, C., Lou, Y.B., Chen, X.B., Samia, A.C.S., Stout, J., and Gole, J.L. (2003). Enhanced nitrogen doping in $TiO_2$ nanoparticles. *Nano Lett*. 3, 1049-1061

Chen, X., Lou, Y., Samia, A. C.S., Burda, C., and Gole, J.L. (2005). Formation of oxynitride as the photocatalytic enhancing site in nitrogen-doped titania nanocatalysts: comparison to a commercial nanopowder. *Adv. Funct. Mater.* 15, 41-49

Chen, H., Nambu, A., Wen, W., Graciani, J., Zhong, Z., Hanson, J.C., Fujita, E., and Rodriguez (2007). Toward photochemical water splitting using band-gap narrowed semiconductors and transition metal based molecular catalysts. *J. Phys. Chem. C.* 111, 1366-1372

Chi, B.; Zhao, L.; Jin, T. (2007). Template-Free Route for Synthesis of Mesoporous N-Doped Titania Spheres. *J. Phys. Chem. C.* 111 (17), 6189-6193

Gratzel, M. (2000). Perspectives for Dye-sensitised nanocrystalline solar cells. *Prog. Photovolt. Res. Appl*. 8, 171-185

Horikawa, T., Katoh, M., and Tomida, T. (2008). Preparation and Characterization of nitrogen-doped mesoporous titania with high specific surface area. *Microporous and Mesoporous Mater.* 110, 397-404

Ihara, T., Miyoshi, M., Iriyama, Y., Matsumoto, O., and Sugihara, S. (2003). Visible light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping. *Appl. Catal., B:Environmental.* 42, 403-409

Irie, H., Watanabe, Y., and Hashimoto, K.J. (2003). Nitrogen-Concentration Dependence on Photocatalytic Activity of $TiO_{2-x}N_x$ Powders. *J. Phys. Chem. B.* 107, 5483-5486

Ito, S., Yoshida, S., and Watanabe, T. (2000). Fabrication and Characterization of Meso-Macroporous Anatase $TiO_2$

Kusumawardani, C., Kartini, I., and Narsito. (2010). Synthesis of Nanocrystalline N-doped $TiO_2$ and Its Application on High Efficiency of Dye-sensitized Solar Cells. *Sci. J. UBU*. (1) 1, 1-8

Kusumawardani, C., Suwardi, Kartini, I., and Narsito. (2012). Synthesis of Visible-light Active N-doped $TiO_2$ Photocatalyst. *Asian. J. Chem*. (24) 1, 2255-2262

Lindgren, T., Mwabora, J.M., Avenanõ, E., Jonsson, J., Hoel, A., Granqvist, C.G., and Lindquist S.E. (2003). Potoelectrochemical and optical properties of nitrogen doped titanium dioxide films prepared by reactive DC magnetron sputtering. *J. Phys. Chem. B.* 107, 5709-5716

Linsebigler, A.L., Lu, G., and Yates, J.T. (1995). Photocatalysis on $TiO_2$ surfaces: principles, mechanisms, and selected results. *Chem. Rev.*, 95, 735-58

Ma T., L.; Akiyama, M.; Abe, E. and Imai, I. (2005). High-Efficiency Dye-Sensitized Solar Cell Based on a Nitrogen-Doped Nanostructured Titania Electrode. *Nano Letter.* 5 (12), 2543–2547

Mills, A. and Hunte, S.L. (1997). An overview of semiconductor photocatalysis. *J. Photochem. Photobio. A: Chem.* 108, 1-35

Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Muller, E., Liska, P., Vlachopoulos, N., and Gratzel, M. (1993). Conversion of light to Electricity by cis-$X_2$Bis(2,2'-bipyridil-4,4'-dicarboxylate) ruthenium(II) charge transfer sensitiser (X = Cl-,Br-, I-, CN- and SCN-). *J. Am.Chem. Soc.* 115, 6382-6390

O'Regan, B., and Gratzel, M. (1991). A lowcost, high-efficiency solar cell based on dye-sensitized colloidal $TiO_2$ films. *Nature,* 353, 737-739

Qiu, X., and Burda, C. (2007). Chemically synthesized nitrogen-doped metal oxide nanoparticles. *Chem. Phys.* 339, 1-10

Rouquerol, F., Rouquerol, J., and Sing, K. (1999). *Adsorption by powders and porous solids:*

*principles, methodology, and applications,* academic Press, San Diego

Sathish, M., Viswanathan, B., Viswanath, R.P., and Gopinath., C. (2005). Synthesis, characterization, electronic structure and photocatalytic activity of nitrogen-doped $TiO_2$ nanocatalyst *Chem. Mater.* 17, 6349-6353

Yanasigawa, K. and Ovenstone, J. (1999) Crystallization of Anatase from Amofphous Titania Using the Hydrothermal Technique: Effects of Starting Material and Temperature. *J. Phys. Chem.*, B, 7781-7787

Zhao, Y., Qiu, X., and Burda, C. (2008). The Effect of Sintering on the Photocataltyc Activity of N-doped $TiO_2$ Nanoparticles. *Chem. Mater.* 112, 762-773